

First-principles Calculation of Superconductivity in Hole-doped LiBC: $T_c = 65$ K

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The lattice dynamical properties of Li_xBC are calculated for several values of x using density functional perturbation theory. We find that the electron-phonon coupling parameter λ increases monotonically with decreasing x to a maximum value of 1.4 for $x = 0.125$ owing to the increasing radius of multiply-nested Fermi surface cylinders. The B-C bond-stretching phonon modes have frequencies which are 28% higher than the equivalent modes in MgB_2 . This combination results in a T_c of about 65 K for $x = 0.5$.

It has been suggested recently that hole doped LiBC may have a superconducting transition temperature similar to or exceeding that of the isostructural compound MgB_2 [1, 2]. Experimental confirmation of this would be of great significance since MgB_2 already has an exceptionally high transition temperature of ~ 40 K. Since the discovery of superconductivity in MgB_2 [3] there has been a flurry of interest in it and compounds with similar features, namely, layered crystals with weak interlayer interactions, a corresponding high density of states at the Fermi energy and strong in-plane covalent bonds which are partially filled [4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17]. LiBC has a hexagonal structure with alternating lithium and boron-carbon planes. Although it is semi-conducting owing to the alternating B-C atoms within each plane [1], the addition of holes, likely to be accomplished by the removal of Li atoms, cause it to become metallic and thus potentially superconducting. To date no such effect has been observed experimentally which is the motivation for this article in which we report a first-principles calculation of the electron-phonon coupling in Li_xBC .

To obtain accurate results we employ a plane wave method with the analytic pseudopotentials of Hartwigsen, Goedecker and Hutter using the parameters quoted in their paper [18]. A kinetic energy cut-off criterion of 24 Hartree was placed on the plane waves to ensure good convergence in terms of basis size. The density functional linear response method of Giannozzi *et al.* [19] was used to calculate the phonon spectra and corresponding self-consistent linearized potentials within the local density approximation [20, 21]. Dynamical matrices and linearized potentials were calculated in the irreducible Brillouin zone on a $4 \times 4 \times 2$ q -point mesh using the ground-state wave functions obtained on a $8 \times 8 \times 4$ k -point mesh. To incorporate hole doping we removed the appropriate number of electrons from the unit cell and added a positive uniform background to maintain charge neutrality. This approximation is justified from the results of Rosner, Kitaigorodsky and Pickett (RKP) [1] who noted an almost rigid shift in the Fermi level with little renormalization of the electronic density of states upon removal of lithium atoms. The phonon spectra and electron-phonon coupling results were calculated for $x = 0.125, 0.25, 0.375, 0.5, 0.625, 0.75$ and 0.875 . We also performed a ground-state calculation on an even denser $16 \times 16 \times 8$ k -point mesh for producing the electron-phonon coupling matrices as well the Fermi surface plots in Fig. 1.

In Fig. 2 we plot the calculated phonon dispersions along high symmetry lines for each doping level. As is evidenced from the lack of singularities in the phonon curves, the material is found to be stable for all doping concentrations within the approximation of a uniform background. The most noteworthy feature in the spectra is the abrupt dip in the topmost branches between the $\Gamma - M$, $K - \Gamma$ and $A - L$ points. As with MgB_2 , these branches have the E_{2g} symmetry character and the dip arises from the exceptionally strong nesting between concentric cylinders [17] of the Fermi surfaces which are oriented in the direction of the c -axis as shown in Fig. 1. These nesting modes correspond to in-plane bond stretching between the boron and carbon atoms. With decreasing x (i.e. increasing doping) the sharpness of the dip becomes less pronounced although the midpoint moves away from the central axis. Also of interest is the level attraction between certain phonon branches for $x < 0.5$. This is reflected in the Fermi surface cylinders which change from being nearly circular for low doping to hexagonal for high doping. This flattening of the sheets results in additional translational symmetries in the effective potential. The C-B bond-stretching modes have phonon frequencies around 1000 cm^{-1} which is considerably higher than the B-B frequencies of MgB_2 which are about 725 cm^{-1} [16].

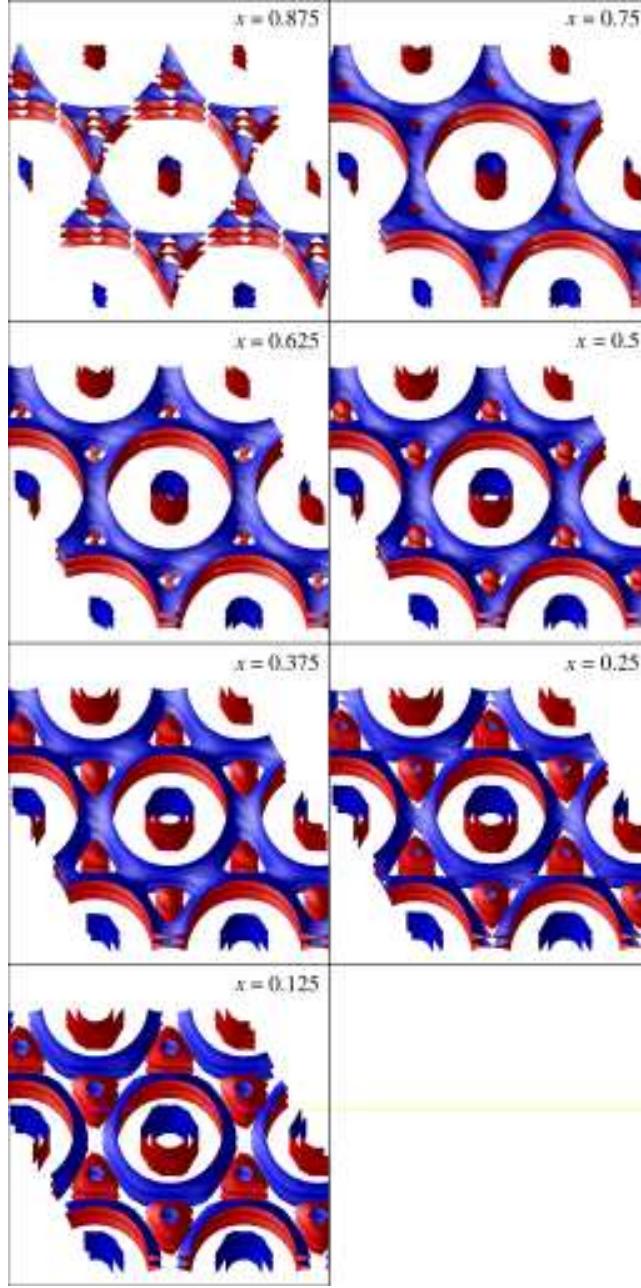


FIG. 1: Fermi surfaces viewed along the c axis for various hole dopings.

The phonon density of states are plotted in Fig. 3. At low doping levels there is a double peak structure between 200 and 400 cm^{-1} as well as peaks at 620 and 1000 cm^{-1} . As the doping level is raised the lower peaks merge together and the higher frequency peaks become much less pronounced. The gap-like structure in the density of states between 400 and 600 cm^{-1} disappears with increased doping.

We now turn to calculation of the superconducting transition temperature. Details of Migdal-Eliashberg theory which is the basis for these calculations can be found in Ref. [22]. The electron-phonon interaction matrix is determined from the linearized self-consistent potential $\delta V_{\mathbf{q}}^{\text{SCF}}$ by

$$g_{\mathbf{k}+\mathbf{q}_v', \mathbf{k}_v}^{\mathbf{q}_j} = \left\langle \phi_{\mathbf{k}+\mathbf{q}_v'} \left| \sum_i \sqrt{\frac{1}{2M_i\omega_{\mathbf{q}_j}}} \mathbf{e}_{\mathbf{q}_j; i} \cdot \delta V_{\mathbf{q}_j; i}^{\text{SCF}} \right| \phi_{\mathbf{k}_v} \right\rangle, \quad (1)$$

where M_i is the mass of the i 'th ion, $\phi_{\mathbf{k}_v}$ is a single-particle state and $\mathbf{e}_{\mathbf{q}_j; i}$ is the eigenvector of phonon mode \mathbf{q}_j and

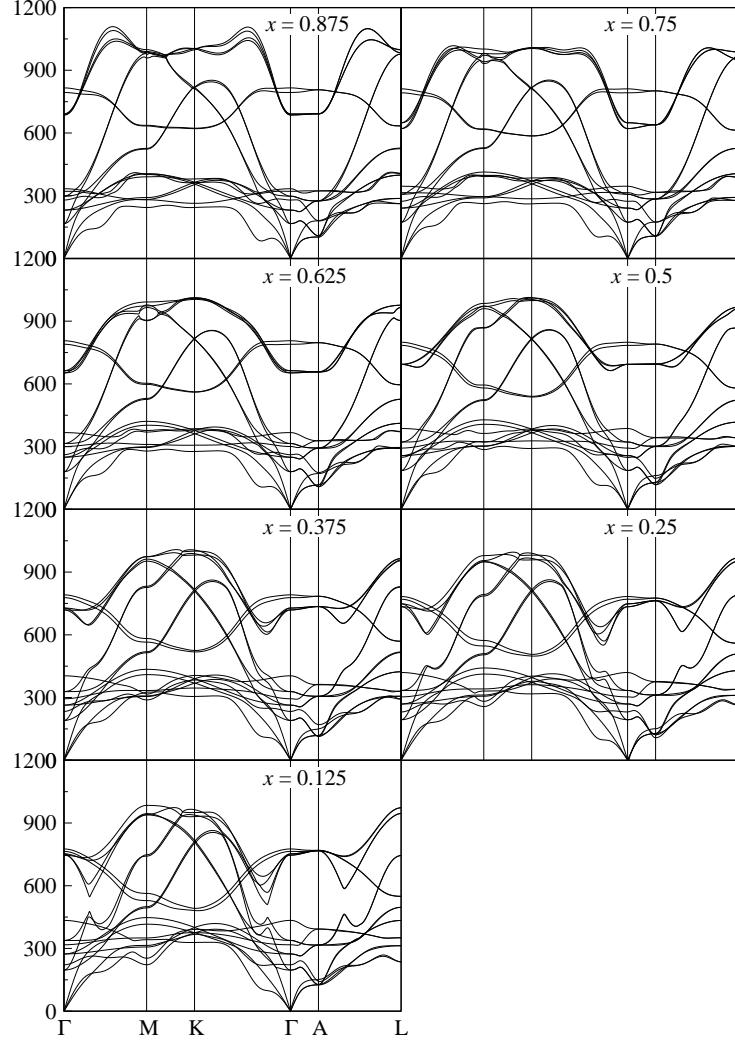


FIG. 2: Calculated phonon dispersions along high symmetry directions for various hole dopings. Frequency units are cm^{-1} .

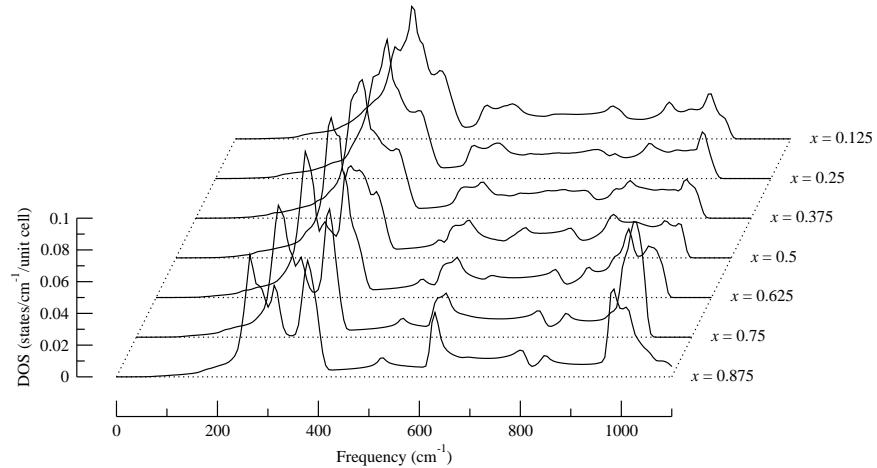


FIG. 3: Calculated phonon density of states for various hole dopings.

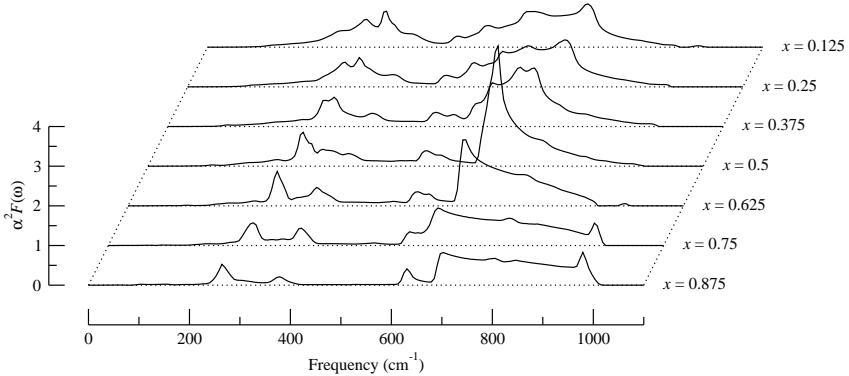


FIG. 4: Calculated electron-phonon spectral function for various hole dopings.

atom i . From this we obtain the phonon linewidth arising from the electron-phonon interaction by averaging over the Fermi surface

$$\gamma_{\mathbf{q}j} = 2\pi\omega_{\mathbf{q}j} \sum_{\mathbf{k}vv'} |g_{\mathbf{k}+\mathbf{q}v',\mathbf{k}v}^{\mathbf{q}j}|^2 \delta(\epsilon_{\mathbf{k}v} - \epsilon_F) \delta(\epsilon_{\mathbf{k}+\mathbf{q}v'} - \epsilon_F), \quad (2)$$

where $\epsilon_{\mathbf{k}v}$ is the Kohn-Sham [23] eigenvalue and ϵ_F is the Fermi energy. The central quantity in superconductivity theory is the electron-phonon spectral function $\alpha^2 F(\omega)$. This can be written in terms of the phonon linewidth by

$$\alpha^2 F(\omega) = \frac{1}{2\pi N_F} \sum_{\mathbf{q}j} \frac{\gamma_{\mathbf{q}j}}{\omega_{\mathbf{q}j}} \delta(\omega - \omega_{\mathbf{q}j}), \quad (3)$$

where N_F is the density of states at the Fermi energy. The total electron-phonon coupling parameter is defined as the first reciprocal moment of $\alpha^2 F(\omega)$

$$\lambda = 2 \int_0^\infty \frac{\alpha^2 F(\omega)}{\omega} d\omega. \quad (4)$$

Finally T_c can be estimated from the McMillan equation [24],

$$T_c = \frac{w_{\log}}{1.2} \exp \left(\frac{-1.04(1 + \lambda)}{\lambda - \mu^*(1 + 0.62\lambda)} \right), \quad (5)$$

with μ^* , the Morel-Anderson pseudopotential, representing Coulombic repulsion and the logarithmic average frequency given by

$$w_{\log} = \exp \left\{ \frac{2}{\lambda} \int_0^\infty \alpha^2 F(\omega) \frac{\ln \omega}{\omega} \right\}. \quad (6)$$

The three main components in determining T_c are therefore the density of states at the Fermi energy N_F , the logarithmic average frequency w_{\log} and the strength of the electron-phonon coupling on the Fermi surface. By plotting $\alpha^2 F(\omega)$ we can gauge the relative strength of the coupling. This is done in Fig. 4. For most phonon-mediated superconductors the phonon density of states and $\alpha^2 F(\omega)$ differ only slightly [25]. This is not the case here: the modes above 600 cm^{-1} which dominate in $\alpha^2 F(\omega)$ are suppressed in the phonon density of states in Fig. 3. This is particularly evident for the peak at $x = 0.5$ and $\omega \approx 600 \text{ cm}^{-1}$ which corresponds to the weakly dispersed E_{2g} branch in the $\Gamma - A$ direction. We plot in Fig. 5 N_F , w_{\log} , λ , and T_c using an empirical value for μ^* of 0.09 which was found to reproduce T_c in MgB₂ [1]. The density of states at the Fermi energy increases sharply from $x = 1$ to $x = 0.75$. Beyond this N_F increases more gradually with a slight upturn at $x = 0.5$ and has values between 15 and 21 states/spin/Hartree/unit cell. As hole concentration is raised w_{\log} drops by about 25% from 802 K at $x = 0.875$ to 608 K at $x = 0.125$. There is also an inflection point at $x = 0.5$ in this curve. The total electron-phonon coupling

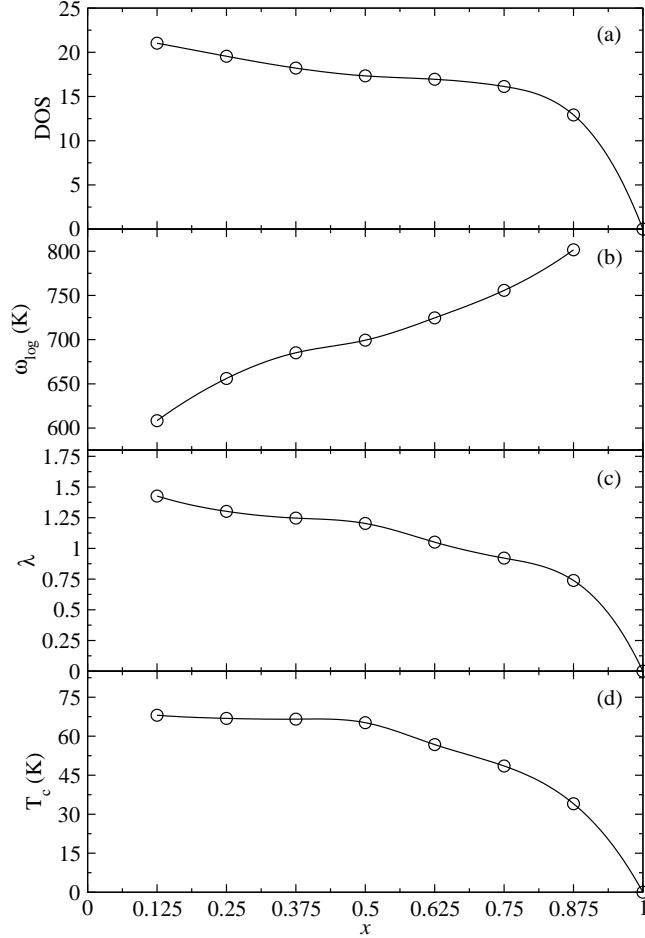


FIG. 5: Properties calculated as a function of Li concentration x : density of states at Fermi energy in units of states/spin/Hartree/unit cell (a), logarithmic average frequency (b), electron-phonon coupling parameter λ (c), and superconducting transition temperature from the McMillan formula (d). The circles represent calculated points and the interpolating lines are cubic splines.

parameter λ increases over the whole range to a maximum value of 1.43. This is a direct result of the increase with $1 - x$ of the Fermi surface nesting vector $2k_F$ which maps the opposing walls of the cylindrical sheets shown in Fig. 1. We again note an inflection point in λ for $x = 0.5$. From proportionality arguments, RKP obtained $\lambda \approx 1.5$ for $x = 0.5$ which is larger than the 1.20 found here. Nonetheless, this is substantially larger than $\lambda = 0.82$ found in MgB₂ [6, 16, 26, 27]. Despite the fairly large increase in λ over the whole range of x , T_c reaches a plateau of 65 K at $x = 0.5$. The reason for this is the drop in ω_{\log} as a function of $1 - x$ which enters as a proportionality in Eq. 5 as well as the saturation of N_F for $x < 0.75$. The highest value for T_c is 68 K at $x = 0.125$, this is substantially higher than that observed for MgB₂ but lower than the ~ 100 K estimated by RKP.

In conclusion, we find from our first-principles calculations that hole-doped LiBC is a superconductor with exceptionally strong in-plane coupling. As with MgB₂ this is due to a small number of phonon modes close to the Γ point which scatter electrons at the Fermi surface from one side of a cylindrical sheet to another. Although the superconducting transition temperature is much higher than in MgB₂, the decrease in the average phonon frequency as the doping concentration is raised limits the potential gain in T_c from the increase in λ and we note that hole doping beyond $x = 0.5$ will not result in any substantial improvement T_c . Nonetheless, going by these results, Li _{x} BC may be an impressive superconductor well worth further investigation.

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- [1] H. Rosner, A. Kitaigorodsky, and W. E. Pickett. *Phys. Rev. Lett.*, 88:127001, 2002.
- [2] P. Ravindran, P. Vajeeston, R. Vidya, A. Kjekhus, and H. Fjellvåg. *Phys. Rev. B*, 64:224509, 2001.
- [3] J. Nagamatsu, N. Nakagawa, T. Muranaka, Y. Zenitani, and J. Akimitsu. *Nature*, 410:63, 2001.
- [4] H. J. Choi, D. Roundy, H. Sun, M. L. Cohen, and S. G. Louie. *Nature*, 418:758, 2002.
- [5] H. Rosner, J. M. An, W. E. Pickett, and S. L. Drechsler. *Phys. Rev. B*, 66:24521, 2002.
- [6] K.-P. Bohnen, R. Heid, and B. Renker. *Phys. Rev. Lett.*, 86:5771, 2001.
- [7] X. L. Chen. *J. Phys. Condens. Matter.*, 13:L723, 2001.
- [8] S. V. Okatov, A. L. Ivanovskii, Y. E. Medvedeva, and N. I. Medvedeva. *Phys. Status Solidi B*, 225:R3, 2001.
- [9] I. R. Shein, N. I. Medvedeva, and A. L. Ivanovskii. *Phys. Solid State*, 43:2213, 2001.
- [10] E. Z. Kurmaev, I. I. Lyakhovskaya, J. Kortus, A. Moewes, N. Miyata, M. Demeter, M. Neumann, M. Yanagihara, M. Watanabe, T. Muranaka, and J. Akimitsu. *Phys. Rev. B*, 65:134509, 2002.
- [11] C. Joas, Eremin, D. Manske, and K. H. Bennemann. *Phys. Rev. B*, 65:132518, 2002.
- [12] G. Profeta, A. Continenza, F. Bernardini, and S. Massidda. *Phys. Rev. B*, 65:54502, 2002.
- [13] P. P. Singh. *Phys. Rev. Lett.*, 87:87004, 2001.
- [14] K. D. Belashchenko, M. van Schilfgaarde, and V. P. Antropov. *Phys. Rev. B*, 64:92503, 2001.
- [15] J. M. An and W. E. Pickett. *Phys. Rev. Lett.*, 86:4366, 2001.
- [16] T. Yildirim, Gülsen, J. W. Lynn, C. M. Brown, T. J. Udoic, Q. Huang, N. Rogado, K. A. Regan, M. A. Hayward, J. S. Slusky, T. He, M. K. Haas, P. Khalifah, K. Inumaru, and R. J. Cava. *Phys. Rev. Lett.*, 87:37001, 2001.
- [17] J. Kortus, I. I. Mazin, K. D. Belashchenko, V. P. Antropov, and L. L. Boyer. *Phys. Rev. Lett.*, 86:4656, 2001.
- [18] C. Hartwigsen, S. Goedecker, and J. Hutter. *Phys. Rev. B*, 58:3641, 1998.
- [19] P. Giannozzi, S. de Gironcoli, P. Pavone, and S. Baroni. *Phys. Rev. B*, 43:7231, 1991.
- [20] D.M. Ceperly and B.J. Alder. *Phys. Rev. Lett.*, 45:566, 1980.
- [21] J. Perdew and A. Zunger. *Phys. Rev. B*, 23:5048, 1981.
- [22] P. B. Allen and B. Mitrovic. Solid state physics. volume 37, page 1. Academic Press, New York, 1982.
- [23] W. Kohn and L. J. Sham. *Phys. Rev.*, 140:A1133, 1965.
- [24] W. L. McMillan. *Phys. Rev.*, 167:331, 1968.
- [25] S. Y. Savrasov and D. Y. Savrasov. *Phys. Rev. B*, 54:16487, 1996.
- [26] Y. Kong, O. V. Dolgov, O. Jepsen, and O. K. Andersen. *Phys. Rev. B*, 64:20501, 2001.
- [27] Amy Y. Liu, I. I. Mazin, and Jens Kortus. *Phys. Rev. Lett.*, 87:87005, 2001.